

FORM PTO-1590 (Modified)
(REV 11-99)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

WLJ.072

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

NEW 09/763641

INTERNATIONAL APPLICATION NO.

PCT/GB00/02301

INTERNATIONAL FILING DATE

26 JUNE 2000

PRIORITY DATE CLAIMED

26 JUNE 1999

TITLE OF INVENTION

METHOD AND APPARATUS FOR FORMING A FILM ON A SUBSTRATE

APPLICANT(S) FOR DO/EO/US

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MACNEIL, John

WILBY, Antony, Paul

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☐ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
- ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
- ☒ A copy of the International Search Report (PCT/ISA/210).
- ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
- ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
- ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
- ☐ A copy of the International Preliminary Examination Report (PCT/PEPA/409).
- ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

UNEXECUTED DECLARATION AND POWER OF ATTORNEY

ABSTRACT OF WO 01/01472 A1

U.S. APPLICATION NO. (IF KNOWN) - SEE 37 CFR 1.53	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
NEW 763641	PCT/GB00/02301	WLJ.072

21. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :	CALCULATIONS PTO USE ONLY
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO	\$1,000.00
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	\$860.00
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO	\$710.00
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims do not satisfy provisions of PCT Article 33(1)-(4)	\$690.00
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)	\$100.00
ENTER APPROPRIATE BASIC FEE AMOUNT =	\$860.00
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30	\$0.00
CLAIMS NUMBER FILED NUMBER EXTRA RATE	
Total claims 27 - 20 = 7 x \$18.00	\$126.00
Independent claims 3 - 3 = 0 x \$80.00	\$0.00
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>	\$0.00
TOTAL OF ABOVE CALCULATIONS =	\$986.00
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). <input type="checkbox"/>	\$0.00
SUBTOTAL =	\$986.00
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30 +	\$0.00
TOTAL NATIONAL FEE =	\$986.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>	\$0.00
TOTAL FEES ENCLOSED =	\$986.00
	Amount to be refunded \$ charged \$

☒ A check in the amount of **\$986.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **50-0238** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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33289
 REGISTRATION NUMBER _____
FEB. 26, 2001
 DATE _____

Katherin GILES et al.

WLJ.072

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of :
Katherine GILES et al. : Attn: Applications Branch
Serial No. [NEW] : Attorney Docket No. WLJ.072
Filed: February 26, 2001 :

METHOD AND APPARATUS FOR FORMING A FILM ON A SUBSTRATE

PRELIMINARY AMENDMENT

Honorable Assistant Commissioner
of Patents and Trademarks,
Washington, D.C. 20231

Sir:

Preliminary to the examination of the above-identified application, please
enter the following amendments and remarks.

IN THE CLAIMS

Please cancel claims 24 and 29 without prejudice.

Please amend claims 3, 4, 6, 8, 10-12, 14-16 and 18-21 as follows:

Claim 3, line 1, delete "or 2".

Claim 4, line 1, change "any preceding claim" to --claim 1--.

Claim 6, line 1, delete "or 2".

Claim 8, line 1, change "any preceding claim" to --claim 1--.

Claim 10, line 1, delete "or claim 7".

Claim 11, line 1, change "any preceding claim" to --claim 1--.

Claim 12, line 1, change "any preceding claim" to --claim 1--.

Claim 14, line 1, change "any preceding claim" to --claim 13--.

Claim 15, line 1, change "any preceding claim" to --claim 13--.

Claim 16, line 1, change "any one of the preceding claims" to --claim 13--.

Claim 18, line 1, delete "or 17".

Claim 19, line 1, delete "or 17".

Claim 20, line 1, delete "or 17".

Claim 21, line 1, delete "or 17".

REMARKS

By this Preliminary Amendment, claims 24 and 29 have been canceled, and claims 3, 4, 6, 8, 10, 11, 12, 14, 15, 16, 18, 19, 20, and 21 have been amended to eliminate multiple dependencies for the purpose of reducing the overall filing fee.

Entry of this Preliminary Amendment is respectfully requested.

Respectfully submitted,

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19/PRTS

09/763641
JC02 Rec'd PCT/PTO 26 FEB 2001

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Method and Apparatus for forming a Film on a Substrate

This invention relates to a method and apparatus for forming a film on a substrate particularly, although not exclusively, to a film which is deposited on a semiconductor silicon wafer with flowing properties and retains carbon-containing groups on setting.

A number of methods have been disclosed for depositing a thin film on a semiconductor wafer, and examples included US 5314724, US 489753, US 5593741, EP-A-0731982 and EP-A-0726599. It can be seen from these that, up until recently, organic-containing silicon precursors have been processed or further processed in such a way as to avoid or subsequently remove organic components from the as-deposited film; this is, for example, disclosed in US 5314724. In addition, for some applications, it has been found to be difficult to retain both good film quality and good gap-fill capability on the surfaces and in recesses of a wafer on which the film is deposited.

According to a first aspect of the present invention, there is provided a method of forming a film on a substrate comprising:

- (a) positioning the substrate on a support in a chamber;
- (b) Supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and
- (c) setting the film such that carbon-containing groups

are retained therein.

The present invention provides a method of forming an unset film. Typically, the film is flowable (that is a film with a degree of surface mobility) and may thus provide good gap fill properties on the substrate.

It should be understood that without affecting the generality of this invention where gap fill properties are not required, e.g. for InterMetal Dielectric (IMD) layers on a semiconductor, then a flowing intermediate film will not be required. However the intermediate film deposited according to this invention will contain OH, which is almost entirely removed by the 'setting' process.

The formation of an OH and CH containing intermediate which is then further processed to remove OH but contain CH enables the formation of improved dielectric layers.

The substrate may be a semiconductor wafer, for example a silicon semiconductor wafer of the type known in the art.

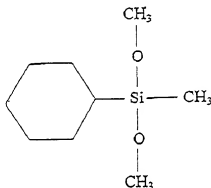
Preferably, the oxidising agent is oxygen, although others could be used, for example H_2O_2 .

For example, the silicon-containing organic compound may be an organosilane or an organosiloxane. Preferably, the silicon-containing organic compound is an alkylsilane, and even more preferably is a tetraalkylsilane. In a particularly preferred embodiment of the invention, the silicon-containing organic compound is tetramethylsilane (TMS). However, for example, other organosilanes or

organosiloxanes could be used, one example being 1,1,3,3-tetramethyldisiloxane (TMDS).

Experiments suggest that methoxysilanes, and in particular methoxymethylsilanes, produce films with very low dielectric constants and may be particularly preferred.

Particularly good results have been achieved with cyclohexyldimethoxymethylsilane (CHDMMS) which has the following structure:



Experiments have also shown that a methoxysilane (e.g. CHDMMS) may be able to be processed as in the above method described, but without any oxidising agent present in the plasma. It is supposed that this is because the Si-O bond already exists as part of the methoxy group.

Accordingly, according to another aspect the invention consists in a method of forming a film on a substrate comprising:

- (a) positioning the substrate on a support in a chamber;
- (b) supplying to the chamber in gaseous or vapour form an organic compound including an Si-O bond to deposit a

film on the substrate; and

(c) setting (e.g. annealing) the film such that carbon-containing groups are retained therein.

Preferably the compound is supplied in the presence of a plasma, but other energy sources may be utilised to cause appropriate deposition and these may be combined with spin-on techniques.

The film may be deposited on a substrate positioned on a low-temperature support for example, a support at a temperature of about 0°C. Indeed temperatures in the range 0°C to 70°C have produced practical results, with temperatures of 30° and 50°C proving particularly practical.

In one embodiment, the method may further comprise supplying RF power during deposition of the film. This RF power is preferably applied to a showerhead or the like through which the gaseous precursors are passed into the chamber.

Whilst any suitable experimental conditions may be used, it has been found that typical conditions include a flow rate of 210 sccm tetramethylsilane, a flow rate of 200 sccm O₂, a chamber pressure of 2000 mT, a support temperature of 0° and a showerhead temperature of 100°C, and 250 watts of 380 khz RF power applied to the showerhead, although it is pointed out that these are only typical conditions.

The setting of the film may be carried out by an

annealing step, for example at a temperature of about 450°C which serves to remove water from the deposited film. It has been found that typical k value of the set film is about 2.55, for example for a 6000Å thick film deposited with a base layer (prior to deposition of the film) or capping layer (on the formed layer) after an annealing step at about 450°C in the absence of oxygen. This k value is a measure of the dielectric constant and it can be seen that the present invention provides a particularly low dielectric constant.

Alternatively, and often preferably, the setting step is performed by exposing the deposited film to an H₂ containing plasma without any prior heating of the film. In this connection it is preferred that the support is not biased during the deposition stage to avoid heating arising from ion bombardment.

According to a third aspect of the present invention, there is provided a method of forming a film on a substrate comprising:

- (a) positioning the substrate on a support in a chamber;
- (b) supplying to the chamber in gaseous or vapour form tetramethylsilane and oxygen in the presence of a plasma and a supply of RF power to deposit a film on the substrate; and
- (c) setting the film such that carbon-containing groups are retained therein.

The setting step can be performed as set out above.

Particularly good results have been achieved with the H₂ plasma treatment without prior heating.

According to a further aspect of the present invention, there is provided an apparatus for forming a film on a substrate, the apparatus comprising:

- (a) a support for the substrate positioned in a chamber;
- (b) means for supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and
- (c) means for setting the film such that carbon-containing groups are retained therein.

The apparatus may, in one embodiment, further comprise means for improving the uniformity of the deposition of the film on the substrate. This may be arranged in the region of, or around, a showerhead and, whilst the applicant is not to be restricted hereby, it is thought that its role in the uniformity of deposition is possibly as a result of providing a site for surface reactions about the surface periphery thus enhancing deposition rate at the edge of the substrate.

Although the invention has been defined above, it is to be understood that it includes any inventive combination of the features set out above or in the following description.

The invention may be performed in various ways and a specific embodiment will now be described, by way of

example, with reference to the accompanying drawings, an in which:

Figure 1 is a schematic view of an apparatus for use in the present invention;

Figure 2 is a Fourier Transform Infra-Red (FTIR) spectrum showing an as-deposited and annealed film according to this invention;

Figures 3(a) and 3(b) are scanning electron micrographs showing the annealed film formed by the present invention;

Figure 4 is a Fourier Transform Infra-Red (FTIR) spectrum for a first process run without oxygen;

Figure 5 is the equivalent FTIR for the process run with oxygen;

Figure 6 is a table showing initial experimental results using standard delivery systems for CHDMMS;

Figure 7 is a table showing experimental results using a syringe pump to deliver CHDMMS;

Figures 8 to 10 are FTIR spectrum relating to certain experiments identified in Figure 7;

Figure 11 shows FTIR plots for film formed from TMS after an anneal (FTM) process and after H₂ plasma processing when no anneal step has occurred;

Figure 12 is a graph of plots showing the affect of an FTM process, a 5 min H₂ plasma and a 10 min H₂ plasma on the thickness and the refractive index of a TMS based film;

Figures 13 to 15 are respective bar graphs indicating

the affects of an oxidising strip on FTM, 5 min H_2 plasma and 10 min H_2 plasma treated TMS + O_2 deposited films;

Figure 16 illustrates the film stress values pre- and post-oxidising strip, after various post film formation treatment regimes;

Figure 17 sets out the dielectric constant of TMS films after various post formation regimes;

Figure 18 is a bar graph comparing the dielectric constant of layers treated by FTM, 5 min, 10 min and 30 min H_2 plasma for a pair of substrates; and

Figure 19 is a SIMS plot for a TMS + O_2 deposited film which has been set with a 5 min H_2 plasma.

Referring to Figure 1, there is shown an apparatus generally at 1 which includes a vacuum chamber 2 having a showerhead 3 and a wafer support or platen 4. The showerhead 3 is connected to an RF source (not shown) to form one electrode, whilst the support 4 if preferably earthed. Alternatively or additionally, the RF source could be connected to the support 4. The showerhead 3 is connected via pipes (not shown) to respective sources of tetramethylsilane and oxygen. The apparatus is generally of the form disclosed in EP-A-0731982, which is incorporated herein by reference. However, a standard (non-duplex) showerhead is normally used. Also shown is an optional uniformity ring 5 arranged around the showerhead 3. This ring 5 plays an active role in the uniformity of deposition of the film on the wafer and may be desirable

for some processes.

In use, the apparatus 1 is arranged to deposit a water and/or OH containing intermediate layer on a wafer which may be flowable and may be used to produce a planar layer or for "gap filling" for applications such as pre-metal dielectric, shallow trench isolation and intermetal dielectric on semiconductor devices. The film is formed by introducing into the chamber tetramethylsilane and oxygen in gaseous or vapour form and reacting them within the chamber. This forms an intermediate layer with a degree of surface mobility even when a plasma is present. It has been found that very small dimensioned gaps can be filled by the process of the present invention. This is not to restrict the invention as often process conditions may yield an intermediate layer containing OH that does not flow but still retains the other characteristics of this invention. The reaction takes place in the presence of a plasma. Subsequently, the film is annealed by heating, preferably in the absence of oxygen and most preferably in the presence of a hydrogen containing plasma.

Example

The precursor tetramethylsilane (TMS) has been applied with various other precursors, a platen temperature of approximately 0°C and RF power of either low (e.g. 380 Khz) or high (e.g. 13.56 Mhz) frequency where indicated. The basic results were as follows:

TMS + H ₂ O ₂	No deposition in the pressure range up to 5,000 mT
TMS + MeSiH ₃ + H ₂ O ₂	Slight increase in carbon content over just MeSiH ₃ + H ₂ O ₂ . Deposition rate ~ 6000 Å/min
TMS + DiH ₄ + H ₂ O ₂	No carbon in the film. Deposition rate ~ 900 Å/min
TMS + H ₂ O ₂ + RF	Deposition rate ~ 400 Å/min. High refractive index
TMS + O ₂ + RF	Deposition rate over 2 micron/min - high carbon content.

A 'preferred' process was then developed consisting of:

210sccm TMS (calculated from fill rate checks)

200sccm O₂

2,000 mT pressure

0° platen temperature and 100°C showerhead temperature

250 watts of 380khz RF power applied to the showerhead.

This yielded a k value of 2.55 (measured by CV techniques) for a 6,000 Å thick film deposited without base or capping after an anneal at approximately 450°C in the absence of oxygen.

Figure 2 shows a FTIR spectrum for an as-deposited and annealed film according to this aspect of the invention. The two spectra are shown overlain on the same diagram for ease of comparison. The as-deposited spectrum is the lower of the two and shows at 6 the characteristic peak of O-H bonds associated with water. Between 3,000 and 2,600 wave

numbers O-H bonds associated with free water, isolated O-H and H bonded O-H are present. Water contains free water and H bonded O-H and thus gives a characteristically broad peak in this area. At 7 is the C-H₃ peak; at 8 is the Si-CH₃ peak (Si-C); and at 9 is the Si-O peak.

It can thus be seen that a film has been deposited containing water and/or OH which is subsequently removed by the annealing step and that CH₃ is present, is bonded to Si and remains in the film after annealing to form the hard film.

Generally, an indicator of low k characteristics is a high Peak Area Ratio(PAR) between Si-C and Si-O on the FTIR. It is believed Si-C bonds block Si-O bonds and thus reduce the density of the resultant film. Hence, a high Peak Area Ratio Si-C:Si-O is indicative of a low k film. It was however noted that for these plasma deposited and annealed films the measured k values were not as low as the Peak Area Ratio Si-C:SiO would suggest from non-plasma deposited low k films deposited from a reaction of methylsilane and peroxide.

Films of this invention as annealed as shown in Figure 3 which demonstrate the flowing characteristics of the as-deposited film.

In general, the following effect of changing the parameters in a process have been observed:

<u>Parameter</u>	<u>Property</u>		<u>Area Ratio</u> <u>CH/SiO</u>	<u>Uniformity</u>
	<u>Refractive</u> <u>Index</u>	<u>FTIR Peak</u> <u>SiC/SiO</u>		
Pressure increase	down	up	up	better
Power increase	none	down	down	better
Nitrogen flow increase	up	down	down	worse
TMS/O ₂ ratio increase	down	up	up	none
Total TMS/O ₂ decrease	none	down	down	none

An experiment has particularly been carried out using cyclohexyldimethoxymethylsilane (CHDMMS). As is reported below this has shown significantly reduced dielectric constants. It is anticipated that benefits will be found from many methoxysilane compounds such as tetramethoxysilane.

The experiments were carried out in a chamber substantially as shown in Figure 1, or in our co-pending British Patent Application 9914879.3, with an electrode gap spacings of 40mm and 20mm and the uniformity ring shield used for non-plasma based processes removed. The CHDMMS was fed into the chamber using a syringe delivery system described in our co-pending British Patent Application No. 9922691.2, which is incorporated herein by reference, as opposed to a traditional low vapour pressure mass flow controller. This was done due to the fact that, as described below, CHDMMS could not be reliably delivered by conventional means as it has a relatively high boiling point (approximately 200°C) compared to most of the other precursor materials investigated in Application 9914879.3.

All processes were run with plasmas applied to the

showerhead. All wafers were 'set' by annealing for typically 30 minutes at approximately 480°C.

The following parameter ranges have been investigated:

Pressure	-	500 mT to 1500 mT
Power (380 kHz)	-	50 W to 750 W
Platen temperature	-	0°C to 70°C
CHDMMS flows	-	0.5 g/min to 1.5 g/min
Oxygen flows	-	0 to 200 sccm
Nitrogen flows	-	0 to 400 sccm
Peroxide flows	-	0 to 0.75 g/min

It will be appreciated that the relative flow rates are particularly relevant to the process. In general higher rates lead to higher deposition rates and thus a broad range of flow rates can achieve similar results. Thus values outside the above ranges may be applicable.

Two particularly preferred process examples are given below: one of these is with oxygen and one is without oxygen.

Process 1 (no O₂)	
Pressure	900 mT
Power	500 W
Platen temperature	50°C
CHDMMS flow	0.85 g/min
Nitrogen flow	200 sccm

Process 2 (with O₂)	
Pressure	900 mT
Power	250 W
Platen temperature	50°C
CHDMMS flow	0.85 g/min
Oxygen flow	50 sccm
Nitrogen flow	150 sccm

The resultant films were annealed and the post anneal results were as follows:

Process 1 (no O₂)	
Deposition rate	17000Å/min
Uniformity (max/min)	± 4%
Refractive index	1.370
Dielectric constant	2.55

Process 2 (with O₂)	
Deposition rate	9500Å/min
Uniformity (max/min)	± 5%
Refractive index	1.340
Dielectric constant	2.25

As can be seen the dielectric constants in each case are desirably low, but the "with oxygen" process is significantly advantageous.

Figures 4 and 5 show the respective FTIR spectra post anneal. It will be seen that they are substantially similar. The feature between 2500 and 2000 in Figure 5 is believed to result from atmospheric (background) CO₂.

In fact, initial experiments were carried out using a CHDMMS source consisting of a PTFE pot within an evacuated aluminium vessel which was heated to 150°C. The pot was connected by gas line to a gas mass flow controller suitable for H₂O with a conversion factor of 1.000. The RF power was applied to the showerhead with a spacing from the wafer of 40mm. The RF was 380khz continuous mode. Results from these experiments are shown in Figure 6. The numbers

in the CHDMMS column are the nominal gas flow as measured by the mass flow controller however stable flows could not be achieved and therefore these results are for near random quantities of CHDMMS being delivered to the process chamber. At this point experimentation was halted until a superior delivery system for this precursor could be developed.

CHDMMS has a boiling point of 201.2°C, and a density of 0.940 g/cc. As it was noted in these experiments that CHDMMS deposits a low k insulator without the addition of an oxidising agent it is therefore possible that it could be delivered as a liquid to a semiconductor wafer without a chamber being required (e.g. by well known 'spin-on' techniques) and then reacted either thermally or by plasma to form a low k ($k < 3$) insulator layer. The apparatus used may in effect deposit a liquid by vaporising the liquid precursor, delivering it as a vapour and then condensing it onto the wafer at a temperature below the boiling point of the precursor at that pressure. It is not yet clear if the reactions to the precursor take place on the wafer or at some other place, depositing reaction products onto the wafer.

Having developed a more suitable liquid delivery system which utilises a syringe pump, further experiments

were carried out as shown in Figure 7. From these experiments preferred processes were developed as further described here. FTIR for runs 13, 14 and 16-23 of Figure 6 respectively are illustrated in Figures 8 to 10.

Further experiments have been carried out using the following conditions:

Pressure: 2500 millitorr
 RF Power at 13.56 Mhz 250 watts/200mm wafer
 Showerhead temperature 100°C
 TMS flow 100sccm (approximately)
 Oxygen flow 100sccm
 Nitrogen flow 500-600sccm

The ratio of TMS (tetramethylsilane) to oxygen is the same as previously (approximately equal quantities), but at half the total flow rates. In this preferred process nitrogen has been used, primarily as a dilutant.

Thermal treatment step ("setting" or "anneal")
 Time 5 minutes
 Pressure 10 torr nitrogen (no oxygen)
 Wafer temperature 400°C approximately

In the process above, where the process platen temperature was varied, the results were as follows

T Rate °C	A/min	Non-Uniformity % max/min	SiC/SiO	FTIR SiH/SiO	CH/SiO	RI av.	Dielectric constant
10	7,778	2.7	0.0608	0.0060	0.0287	1.3823	2.72
20	7,673	3.8	0.0594	0.0057	0.0280	1.3832	2.72
30	7,589	4.8	0.0588	0.0059	0.0282	1.3791	2.65
45	7,543	3.1	0.0584	0.0056	0.0273	1.3867	2.70
55	not recorded		0.0527	0.0044	0.0234	not recorded	2.75
60	6,968	3.9	0.0512	0.0074	0.0293	1.3935	2.69

Once more the initial deposition process puts down a water and/or OH containing intermediate film which needs to be set to substantially remove the water and/or OH to create a low k layer. For the purposes of the above

experiment this setting was achieved by a thermal treatment step as indicated. However other post deposition processes have been experimented with, as can be seen below. The significant features of this experiment were both the continued achievement of a dielectric constant below 3 and the observation that both the refractive index (which is believed to be a measurement of density) and the dielectric constant dipped when a platen temperature of 30° was used. These results are consistent with the normal understanding that dielectric constant and density are related for a specific film composition, so that lower refractive index will normally indicate a lower dielectric constant.

Subsequent to this experiment a further set of films were formed using the following process matrix:

- | | | | |
|----|----------------------|---------------------------|------------------------------------|
| 15 | • TMS | - | 100 sccm |
| | • O2 | - | 100 sccm |
| | • N2 | - | 600 sccm |
| | • Pressure | - | 2000 mT |
| | • Substrate support- | 30°C, DC ground potential | |
| 20 | | (unbiased) | |
| | • Power | - | 250 Watts High Frequency 13.56 MHz |
| | | | to the showerhead |

The films resulting from this process were set either by the annealing process (which is hereinafter referred to

as FTM treatment) or process and/or by treating the film with an H₂ plasma treatment.

The FTM process was as follows:

- Wafer temperature 450°C
- 5 • Pressure 10 Torr (Nitrogen)
- Time 3-5 minutes

The H₂ plasma treatment was as follows:

- Hydrogen - 1000 sccm
- Pressure - 4000 MT
- 10 • Temperature - 400°C
- Power - 2000 Watts High Frequency 13.56 MHz
to an electrode opposed the wafer
- Time - Depends on thickness but typically 3
minutes for 6kÅ although longer times
15 appear to lead to lower K.

Alternatively other RF frequencies could be used applied to any electrode or electrodes either internal or external to the wafer containing chamber such as to create or sustain ionised hydrogen species adjacent to the film to be
20 treated. This is to include remote plasma sources including microwave and inductively completed RF sources wherever situated.

The H₂ plasma may also contain other components e.g. effectively inert dilutants for example argon, helium or

other gasses or vapours that do not detract from this treatment.

Figure 11 shows respective FTIR plots for the film prepared as described above and then treated by FTM or by plasma. Beneath each chart is an indication of the bonding ratios between various components. As will be understood by a man skilled in the art the slope of the graph is not relevant in a FTIR plot; it is only the peaks which provide information. The relative heights of the peaks are indicated by the ratio tables and it will be seen that there is a significant reduction in the bonding between the various components in a plasma treated film as compared with one that has had the FTM post deposition treatment. This indicates that the hydrogen plasma treated intermediate film is structurally different from the FTM treated intermediate film.

In Figure 12 the upper plot indicates that there is no significant difference in film thickness between the various post treatment processes, but there is a significant driving up of the refractive index the longer a plasma treatment takes place. Indeed after a 10 minute H_2 plasma, the refractive index is approaching that of pure SiO_2 . Normally, as has been explained above, this would be expected to result in a significant increase in dielectric

constant, but as can be seen in Figure 17 an increase in the period of the H_2 plasma treatment simultaneously produces a significant decrease in the dielectric constant, provided that the film is not subject to heat treatment prior to the plasma treatment. Thus after a 10 minute H_2 plasma treatment the OH containing film is set and has a dielectric constant of below 2.2, which is an extremely low figure typically unachievable by chemical vapour deposition means.

It will be noted that a very short H_2 plasma treatment (e.g. 1 minute) does not render the film totally stable nor does it reduce significantly the dielectric constant below an FTM anneal although the film is still comparable with other reported films. Wet etch rate experiments have demonstrated that the hydrogen plasma treatment starts at the top of the film. The longer the plasma process, the greater the depth treated the lower the k value of the treated film. The hydrogen plasma treated film etches considerably (e.g. 20 or more times) slower than the FTM treated film. It will also be observed that an H_2 plasma treatment is also not effective in reducing dielectric constant after a previous heating or anneal step.

Turning now to Figures 13, 14 and 15 it will be seen in Figure 13 that film which has had the FMT treatment

appears to be very susceptible to an oxidising process e.g. a photoresist strip with carbon and hydrogen seemingly being removed from the material. This is not totally surprising, because such an oxidising process was previously used to remove such materials in the film (in particular organics from precursors) before it was appreciated that they might have a beneficial affect on the dielectric constant. Figures 14 and 15, on the other hand, show that the plasma treated films are substantially unaffected by the oxidising photoresist strip process. This is of course important, because it makes it much easier to remove resist from the surface of the dielectric layer without damaging that layer. Figure 16 shows that the plasma treated films also have particularly low stress values whether before or after the oxidising strip.

It is believed that similar results would be achieved with most flowable or water and/or OH containing films that retain carbon, more particularly CH, in the finally used dielectric layers.

Thus the inventors have, in particular determined a process for depositing a flowable or at least OH containing intermediate film which is subsequently set using heat in the absence of oxygen and preferably in the presence of an H_2 containing plasma with the result that the film has a

dielectric constant below 3 and, with the application of hydrogen plasma, a reduced dielectric constant and a good resistance to oxidising strip. It is postulated that this combination results from the surprising fact that H₂ treatment reduces the dielectric constant whilst increasing the refractive index and hence, almost certainly the density as evidenced by a greatly reduced wet etch rate.

Further evidence for this is illustrated in Figures 18 and 19. Figure 18 shows that progressive treatment by H₂ plasma drives down the dielectric constant, with samples treated for 30 minutes achieving a k of 1.8.

Figure 19 provides analysis of the hydrogen plasma treated film has been carried out as follows:

SIMS (secondary ion mass spectrometry) data of a TMS + O₂ deposited film that has been hydrogen plasma treated for 5 minutes has been generated. [The horizontal axis is through the depth of the sample starting at just above the surface and ending in the silicon wafer. What is shown is an organic contaminated (high C) sample surface (to be ignored), followed by a 'true' analysis].

The SIMS profile shows a film surface depleted of carbon and hydrogen by the hydrogen plasma treatment. This is a not unsurprising result and is consistent with a measurable difference in the dielectric constant of this

surface layer and the bulk of the film. When this surface is etched away the remainder of the film (adjusted for its reduced thickness) has a lower dielectric constant than the whole of the film including this surface layer. Yet the whole film including this carbon depleted surface has a lower k value than an FTM treated film.

Wet etch rate experiments show that the hydrogen plasma treatment commences at the upper surface and progresses through the film. The hydrogen plasma treated film wet etches considerably more slowly than an FTM treated film and thus provides clear evidence that depth of treatment increases with plasma treatment times.

It is postulated that the hydrogen plasma treatment effectively replaces Si-CH_3 in the film with $\text{Si-CH}_2\text{-Si}$ (by intermediate reactions in which hydrogen ions and radicals play a part) with increased Si-Si linkage responsible for the increase in the refractive index.

CLAIMS

1. A method of forming a film on a substrate comprising:
 - (a) positioning the substrate on a support in a chamber;
 - (b) supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and
 - (c) setting the film such that carbon-containing groups are contained therein.
2. A method according to claim 1, wherein the oxidising agent is oxygen.
3. A method according to claim 1 or 2, wherein the silicon-containing organic compound is an alkylsilane.
4. A method according to any preceding claim, wherein the silicon-containing organic compound is a tetraalkylsilane.
5. A method according to claim 4, wherein the silicon-containing organic compound is tetramethylsilane.
6. A method according to claim 1 or 2, wherein the silicon-containing organic compound is a methylsilane.
7. A method according to claim 3, wherein the silicon-containing organic compound is cyclohexyldimethoxymethylsilane.

8. A method according to any preceding claim, wherein the film is deposited on a substrate positioned on a low temperature support.

9. A method according to claim 6, wherein the support is at a temperature between about 0°C to about 60°C.

10. A method according to claim 6 or claim 7 wherein the support is at about 30°C,

11. A method according to any preceding claim, further comprising providing a plasma during deposition of the film.

12. A method according to any preceding claim, wherein the set film has a dielectric constant of about 2.55 or less.

13. A method of forming a film on a substrate comprising:

(a) positioning the substrate on a support in a chamber.

(b) supplying to the chamber in gaseous or vapour form tetramethylsilane and oxygen in the presence of a plasma to deposit a film on the substrate; and

(c) setting the film such that carbon-containing groups are contained therein.

14. A method according to any preceding claim, further comprising supplying the plasma from an RF power source connected to an electrode opposing the substrate support.

15. A method according to any preceding claim wherein the substrate support is at D.C. ground during the application of the plasma.
- 5 16. A method as claimed in any one of the preceding claims wherein the film is set by exposing it to an H₂ containing plasma without any prior annealing or heating step.
- 10 17. A method as claimed in claim 16 wherein the H₂ containing plasma is substantially only a H₂ plasma.
18. A method as claimed in claim 16 or 17 wherein the H₂ containing plasma treatment last for between 30 seconds and 30 minutes.
- 15 19. A method as claimed in claim 16 or 17 wherein the H₂ containing plasma treatment lasts from 1 to 10 minutes.
- 20 20. A method as claimed in claim 16 or 17 wherein the H₂ containing plasma treatment step lasts no more than 5 minutes.
21. A method as claimed in claim 16 or 17 wherein the H₂ containing plasma treatment step lasts no more than 10 minutes.
22. A method as claimed in claim 16 where the hydrogen containing plasma is applied simultaneously with heating.

23. A method as claimed in claim 22 where the substrate is heated to approximately 400°C.

24. A method substantially as hereinbefore described with reference to the accompanying drawings and examples.

5 25. A method as claimed in claim 1 where the setting of the film substantially removes water and/or OH peaks from the FTIR spectra of the as deposited film.

26. An apparatus for forming a film on a substrate, the apparatus comprising:

- 10
- (a) a support for the substrate positioned in a chamber;
 - (b) means for supplying to the chamber in gaseous or vapour form a silicon-containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate; and
 - 15 (c) means for setting the film such that carbon-containing groups are contained therein.

27. An apparatus according to claim 26, further comprising means for improving the uniformity of the deposition of the film on the substrate.

20 28. An apparatus according to claim 27, wherein the means for improving the uniformity is arranged around a showerhead.

29. An apparatus substantially as hereinbefore described with reference to, and as illustrated in, the accompanying drawings.

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Abstract

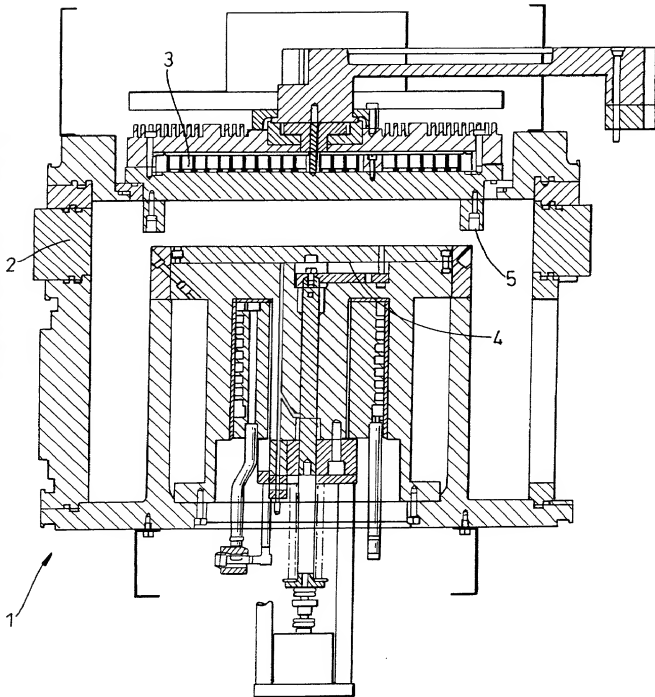
Method and Apparatus for forming a film on a substrate.

5 This invention relates to a method and apparatus for forming a film on the substrate. The method comprises supplying to the chamber in gaseous or vapour form a silicon containing organic compound and an oxidising agent in the presence of a plasma to deposit a film on the substrate and setting the film such that carbon containing groups are retained therein. In particular embodiments the setting is achieved by exposing the film to H_2 plasma.

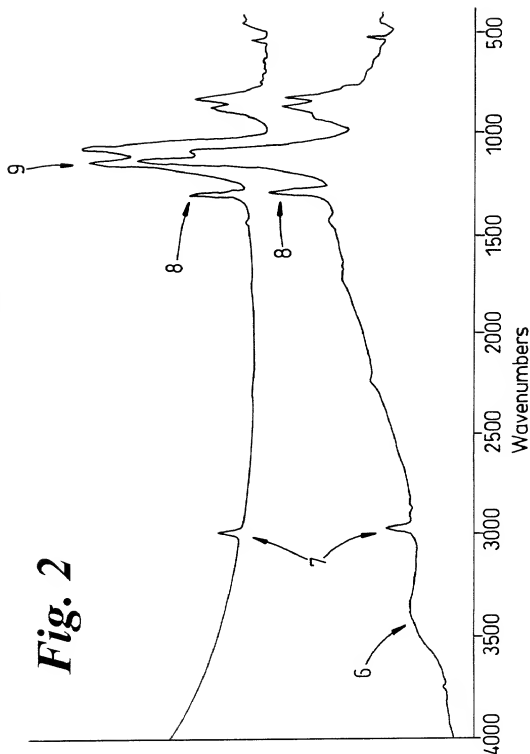
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Figure 1.

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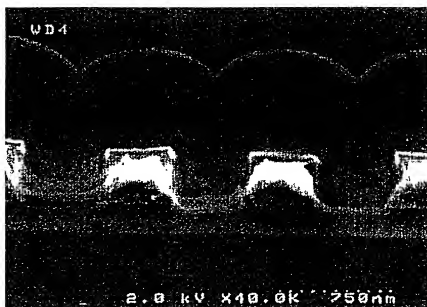
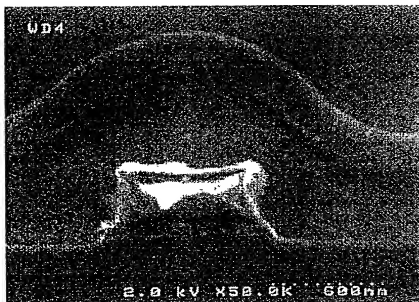
*Fig. 1*

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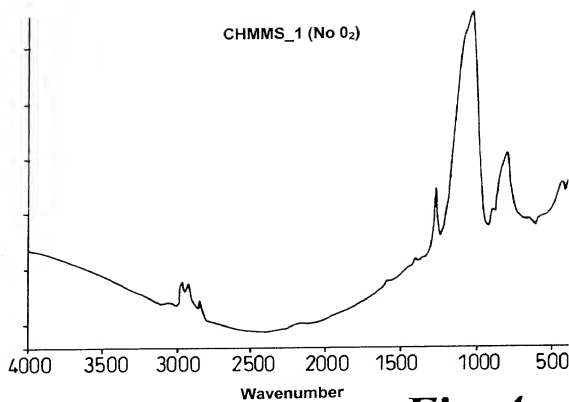
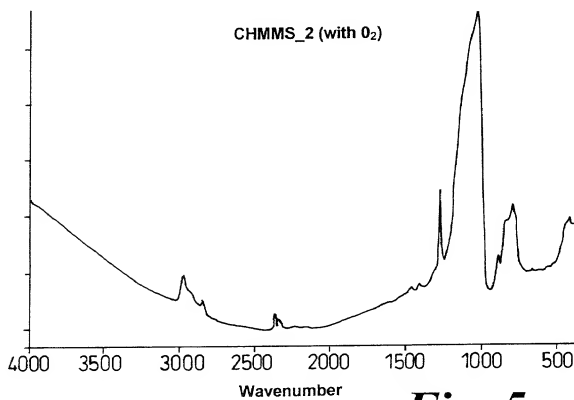


210 / 200 TMS/O₂ 2000MT 250 W 0°C PLATEN PRE AND POST ANNEAL

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*Fig. 3(a)**Fig. 3(b)*

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*Fig. 4**Fig. 5*

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Date	Run No	CHMMMS	H ₂ O ₂	O ₂	N ₂	RF Power (W)	Pressure (mT)	Platen (°C)	Sthead (°C)	Dep rate (Å/min)	Uniformity	RJ	RJ Range	SiC/SiO	SiH/SiO	CH/SiO	K
10/05/99	1	1000	0.75	0	0	50	1500	70	100	1166	6.6	1.482	0.0007				
	2	1300	0.75	0	0	50	900	70	100	681	5.1	1.3702	0.0074				
	3	1300	0.7	0	0	100	900	70	100	2542	6.5	1.3321	0.01				
	4	1300	0.7	0	0	100	900	70	100	1853	6.1	1.3676	0.015				
	5	1300	0.7	0	0	100	900	70	100	1450	8.5	1.3498	0.0125				
	6	1300	0.7	0	0	100	900	70	100	3916	8.1	1.4736	0.0023				
	7	1300	0.7	0	0	100	900	70	100	2008	8.3	1.3587	0.0075				
	8	1300	0.7	0	0	100	900	70	100	3965	22.1	1.5007	0.005				
	9	1300	0.7	0	0	100	900	0	100	2037	22.5	1.3749	0.005				
	10	1300	0.7	0	0	200	900	5	100	1392	13.5	1.4871	0.005				
	11	1300	0.7	0	0	200	900	0	100	716	13.9	1.374	0.005				
Pot Refilled 24/05/99	12	800	0.5	0	0	100	900	70	100	1731	15.9	1.4618	0.0163	0.0343	0	0.1062	
	13	800	0.4	0	0	500	900	70	100	9938	35	1.458	0.0156	0.0191	0	0.0059	
	14	800	0.4	0	0	250	900	70	100	2166	16.2	1.4569		0.0183	0.0063	0.1102	
	15	800	0	0	0	500	900	70	100	-10000	-30	1.45		0.0316	0.021	0.1715	
	16	800	0	0	0	250	900	70	100	-6000	-45			0.0299	0.0365	0.2756	
	17	800	0	0	0	250	900	70	100					0.0322	0.0376	0.303	
	18	800	0	0	0	250	900	70	100	5200						2.55	
	19	800	0	0	0	250	900	70	100	7200						2.52.7	
	20	800	0	0	0	250	900	40	100	5338	23.4	1.4938		0.03	0.039	0.2353	
	21	800	0	0	0	250	900	40	100	4200						3.2	
	22	800	0	0	0	250	900	20	100	3641	14.4	1.4913		0.0396	0.027	0.237	
	23	800	0	0	0	250	900	20	100	6500			0.015			2.87	

Fig. 6

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Flowfill chamber depositions using Cyclohexyldimethoxymethylsilane

P727 - Flowfill chamber (Flow_1), 40mm electrode gap - Syringe delivery system

Process Parameter

Bulk Film Properties

Run Number	CHMMS (g/min)	O ₂ Flow (sccm)	N ₂ Flow (sccm)	Pressure (mT)	Power (W)	Showerhead (°C)	Platen (°C)	Dip rate (Å/min)	Uniformity (%)	Refractive Index	Dielectric Constant	FIR P.A.R. SIC/SIO ₂ /SH/SIO	Comment
1	0.85	0	0	900	250	100	50	7224	10.8	1.4819		0.0357 0.0111 0.1347	Agit 100min - Bright 5min
2	0.65	0	0	900	250	100	50					0.0345 0.0286 0.03872	Peeked off in FTS
3	0.65	0	100(1+8)	900	250	100	50	6190	6.5	1.4875		0.039 0.0415 0.1545	Plasma dark red
4	0.85	0	50(1+3)	900	250	100	50	5810	22.8	1.4815		0.0354 0.0289 0.2489	Purple Plasma
5	0.85	0	50(1+3)	900	250	100	50	8289	13.1	1.51		0.0384 0.0107 0.131	
6	0.65	0	50(1+8)	900	250	100	50	8909	4.47	1.5089		0.0379 0.0139 0.1238	
7	0.85	0	100(1+8)	900	250	100	50	7172	9.2	1.4712		0.0364 0.0172 0.1886	
8	0.65	0	100(1+8)	900	250	100	50	2769	9.2	1.4712		0.0349 0.0387 0.3516	RI wafer
9	0.85	0	100(1+8)	900	500	100	50	12748	3.4	1.489			
10	0.85	0	100(1+8)	900	500	100	50	14222	1.77	1.538			
11	0.85	0	200(1)	900	500	100	50	14192	1.5	1.5228			
12	0.85	0	200(8)	900	500	100	50	14282	1	1.5444			
13	0.85	0	100(1+8)	500	900	100	50	9790	3.7	1.4895			RI wafer
14	0.85	0	200(1+3)	500	900	100	50	11382	6.2	1.4668			RI wafer
15	0.85	0	100(1+8)	900	250	100	50	18116	5.6	1.4634			RI wafer
16	0.65	0	100(1+8)	900	250	100	50	10242	8.3	1.4598			K=2.4 post oven anneal
17	0.85	0	100(1+8)	900	250	100	50			3*			K=2.4 post oven anneal
18	0.85	0	200(8)	900	500	100	50			2.3*			Left overnight before measurement
19	0.85	0	100(1+8)	500	500	100	50			2.9*			K=4.35 post oven anneal
20	0.85	0	100(1+8)	900	500	100	50			3.01*			
21	0.85	0	100(1+8)	900	500	100	50	7869	7.8	1.5144			Grainy film, 5min FTS
22	0.85	0	100(1+8)	900	500	100	50	15897	5.7	1.537			5min FTS
23	0.85	0	100(1+8)	900	500	100	50	14751	3.5	1.4737			5min FTS
24	0.85	0	100(1+8)	900	500	100	50	14343	0.9	1.4737			10min FTS
25	0.85	0	100(1+8)	900	500	100	50	14079	1.6	1.4582			30min FTS
26	0.85	0	100(1+8)	900	500	100	50	18854	4.5	1.4332			5min FTS
27	0.85	0	200(8)	900	250	100	50	1641	6.2	1.4327			5min FTS
28	0.85	0	200(8)	900	250	100	50	1161	6.2	1.4327			5min FTS
29	0.85	0	200(8)	900	500	100	50	15585	3.6	1.4953			5min FTS
30	0.85	0	200(8)	900	500	100	50	14807	3.1	1.4575			5min FTS
31	0.85	0	200(8)	900	750	100	50	16898	3.8	1.503			5min FTS
32	0.85	0	200(8)	900	250	100	50	11658	11.5	1.469	2.56	0.0342 0.0338	Dipped with 30min FTS + Cap
33	0.85	0	200(8)	900	500	100	50			2.66			Dipped with 30min FTS
34	0.85	0	200(8)	900	500	100	50						5min FTS
35	0.85	0	200(8)	900	500	100	50	17106	3.7	1.4552		0.0309 0.0199	5min FTS
36	0.85	0	200(8)	900	500	100	50	17184	3.7	1.459		0.031 0.0292	5min FTS
37	0.85	0	200(8)	1200	500	100	50	2485	2.2	1.5516		0.0311 0.0196	5min FTS
38	0.85	0	200(8)	600	500	100	50	8953	4.6	1.506		0.0333 0.018	5min FTS
39	0.85	0	200(8)	600	250	100	50	7128	0.87	1.5098		0.0349 0.0183	5min FTS
40	0.85	50	150(8)	900	250	100	50	8652	3.8	1.4575		0.0245 0.0242	5min FTS
41	0.85	50	150(8)	900	500	100	50	18448	3.8	1.4209		0.0203 0.009	Femt powder showerhead pattern

Fig. 7 (Part 1 of 3)

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09/763641

Run Number	CHHMS (g/min)	O ₂ Flow (Sccm)	N ₂ Flow (Sccm)	Pressure (nT)	Power (W)	Showerhead (°C)	Pidant (°C)	Uniformity (%)	Refractive Index	Dielectric Constant	SCISO	FTIR/PAIR SHISO	CHISO	Comment
42	0.85	50	250(8)	900	250	100	50	-1.8um	-	-	0.0209	0.0058	0.0572	Entire film cloudy
43	0.85	50	200	900	500	100	50	17898	5.7	1.3978	0.0161	0.003	0.0356	Powder stripes
44	0.85	50	150(8)	900	1000	100	50	17898	8.4	1.2031	0.0348	0.0083	0.0588	Fuzzy powder
45	0.85	0	200(8)	600	250	100	50	8213	3.4	1.4609	0.0318	0.004	0.2169	RI Water
46	0.85	0	200(8)	600	250	100	50	9912	8.2	1.4649	-	-	RI Water	RI Water
47	0.85	0	200(8)	1200	100	100	50	1792	29.2	1.4635	-	-	-	No FTS
48	0.85	0	200(8)	600	250	100	50	10233	3.3	1k	0.0387	0.0316	0.3823	5min FTS, no cap
49	0.85	0	200(8)	600	250	100	50	-	-	2.56	-	-	-	5min FTS, no cap
50	0.85	0	200(8)	600	250	100	50	-	-	2.72	-	-	-	Wafer thin, 1st of day, 5min FTS, Cap
51	0.85	0	200(8)	900	250	100	50	-	-	3.16	-	-	-	No FTS
52	0.85	0	200(8)	900	250	100	50	-	-	2.33	-	-	-	30min FTS, Cap
53	0.85	0	200(8)	600	250	100	50	13034	5.7	1k	0.0391	0.0532	0.3933	No FTS
54	0.85	0	200(8)	900	250	100	50	13829	5.7	1k	0.0368	0.0135	0.3965	No FTS
55	0.85	0	200(8)	900	250	100	50	11131	7.7	1k	0.0376	0.0161	0.0765	30min FTS
56	0.85	0	200(8)	900	250	100	50	9809	4.9	1k	0.0363	0.0082	0.0583	80min FTS
57	0.85	0	200(8)	900	250	100	50	9853	3.4	1k	2.62	-	-	5min FTS, no cap
58	0.85	0	200(8)	900	250	100	50	-	-	2.52	-	-	-	30min FTS, no cap
59	0.85	0	200(8)	900	250	100	50	-	-	2.52	-	-	-	80min FTS, no cap
60	0.85	0	200(8)	900	250	100	50	13020	8.1	1.3581	0.0374	0.0551	0.3939	No FTS
61	0.85	0	200(8)	900	250	100	50	13683	5.2	1.4283	0.0367	0.0573	0.3911	No FTS
62	0.85	0	200(8)	900	250	100	50	12450	5.2	1.4283	0.0322	0.02	0.2575	5min FTS @500°C
63	0.85	0	200(8)	900	250	100	50	11885	4.2	1.4466	0.0373	0.0162	0.1847	5min FTS @500°C
64	0.85	0	200(8)	900	250	100	50	10879	1.37	1.5553	0.0373	0.0162	0.109	5min FTS @500°C
65	0.85	0	200(8)	900	250	100	50	-	-	2.93	-	-	-	5min FTS @500°C no cap
66	0.85	0	200(8)	900	250	100	50	-	-	2.61	-	-	-	5min FTS, cap @500°C
67	0.85	0	200(8)	900	250	100	50	-	-	2.61	-	-	-	5min FTS, cap @500°C
68	0.85	0	200(8)	900	250	100	50	-	-	2.52	-	-	-	60min FTS
69	0.85	0	200(8)	900	500	100	50	17388	4.2	1.4207	0.0323	0.0103	0.0825	60min FTS
70	0.85	0	200(8)	900	500	100	50	17484	3.8	1.4146	-	-	-	60min FTS, cap
71	0.85	0	200(8)	900	500	100	50	-	-	2.55	-	-	-	60min FTS, cap
72	0.85	0	200(8)	900	500	100	50	-	-	2.53	-	-	-	5min FTS (centre cracks)
73	0.85	0	200(8)	900	250	100	50	9899	4.3	1.4518	0.0308	0.0073	0.0635	5min FTS (centre cracks)
74	0.85	50	150(8)	900	250	100	50	9554	4.2	1.3707	0.0298	0.0084	0.0403	30min FTS, cap
75	0.85	50	150(8)	900	250	100	50	-	-	2.26	-	-	-	30min FTS, cap
76	0.85	0	200(8)	900	250	100	50	13971	8	1.4022	-	-	-	RI Water
77	0.85	0	200(8)	900	250	100	50	12355	8.3	1.4308	-	-	-	RI Water
78	0.85	50	150(8)	900	250	100	50	11628	6.1	1.4115	-	-	-	RI Water
79	0.85	50	150(8)	900	250	100	50	11070	6.9	1.3942	-	-	-	RI Water
80	0.85	0	200(8)	900	500	100	50	25340	7.4	1.4493	-	-	-	RI Water
81	0.85	0	200(8)	900	500	100	50	22157	6.5	1.4307	-	-	-	RI Water
82	0.85	0	200(8)	900	500	100	50	19912	3.4	1.4358	-	-	-	5min FTS
83	0.85	0	200(8)	900	500	100	50	17632	2.4	1.4308	-	-	-	5min FTS
84	0.85	0	200(8)	900	500	100	50	14636	2.4	1.4463	-	-	-	5min FTS
85	0.85	0	200(8)	900	500	100	20	21774	5.8	1.5393	-	-	-	30min FTS
86	0.85	0	200(8)	900	500	100	20	-	-	-	-	-	-	30min FTS (peeled off)
87	0.85	0	200(8)	900	500	100	20	-	-	-	0.0348	0.0371	0.079	30min FTS (peeled off)
88	0.85	0	200(8)	900	500	100	20	-	-	2.43	0.0348	0.0748	0.0748	60min FTS (peeled off)

Fig. 7 (Part 2 of 3)

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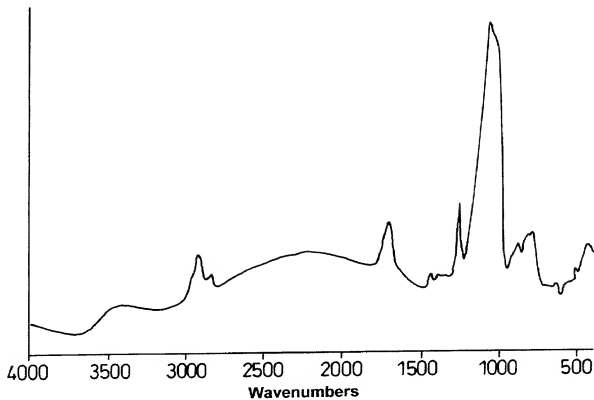
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Run Number	CHMAS (g/min)	O ₂ Flow (Sccm)	N ₂ Flow (Sccm)	Pressure (mT)	Power (W)	Showhead (°C)	Platen (°C)	Dig rate (Å/min)	Uniformity (%)	Reflective Index	Dielectric Constant	SICSO	SICSO	FIR P.A.R. SICSO	CHSIO	Comment
80	0.85	0	200(8)	900	500	100	17344	2.4	17344	1.4129		0.0341	0.0103	0.0103	0.1051	
81	0.85	25	175(8)	900	500	100	50	17840	1.9	1.4388		0.0327	0.0078	0.0078	0.0776	Faint powder sth
82	0.85	50	150(8)	900	250	100	50	9278	2.4	1.3875		0.0303	0.0078	0.0078	0.0776	Small amount of centre cracking
83	0.85	50	0	900	500	100	50	9663	5.9	1.3946		0.0344	0.0078	0.0078	0.0532	Massive centre cracking
84	0.85	50	0	900	500	100	50	~10000				0.0773	0.0078	0.0078	0.0776	
85	0.85	50	150(8)	900	250	100	50	21408	4.6	1.4199	2.49					30min FTS, cap
86	0.85	50	150(8)	900	250	100	50				2.48					30min FTS, cap
87	0.85	25	175(8)	900	250	100	50	9917	8.8	1.4521	2.48	0.0342	0.0093	0.1091	0.1091	30min FTS, cap
88	0.85	25	175(8)	900	250	100	50	3846	11.7	1.4582	2.47	0.0334	0.0117	0.1441	0.1441	30min FTS, cap
89	0.85	25	175(8)	900	250	100	50				2.45					5min FTS, cap
90	0.85	25	175(8)	900	250	100	50				2.45					30min FTS, cap
91	0.85	25	175(8)	900	250	100	50				2.45					30min FTS, cap
92	0.85	25	175(8)	900	250	100	50	12080	7.6	1.5107		0.0238	0.0093	0.0093	0.0093	5min FTS Showerhead dots
93	0.85	0	100(8)	900	500	100	50	12502	5.1	1.5081		0.025	0.0119	0.0119	0.0119	5min FTS Showerhead dots
94	0.85	0	100(8)	900	500	100	50	20470			2.9	0.0282	0.0148	0.0148	0.0148	30min FTS cap
95	0.85	0	400(8)	900	750	100	50	34742				0.0278	0.0148	0.0148	0.0148	30min FTS
96	0.85	0	400(8)	900	750	100	50	13830	2.4	1.486						30min FTS
97	0.85	0	400(8)	900	750	100	50				2.72					30min FTS CAP
CHAMBER SPACING CHANGED TO 20MM																
108	0.85	0	200(8)	900	500	100	50	17626		1.3437						30min FTS
109	0.85	0	200(8)	900	500	100	50	21765	8.4	1.3654						30min FTS, RI Wafer
110	0.85	25	175(8)	900	250	100	50	11438	17.6	1.3713						30min FTS
111	0.85	25	175(8)	900	250	100	50	12828	13.6	1.3898						30min FTS, RI Wafer
112	0.85	0	200(8)	900	500	100	50	12828	11.6	1.3898						30min FTS, RI Wafer
113	0.85	0	200(8)	900	500	100	50	12185	3.4	1.3756						30min FTS
114	0.85	0	200(8)	400	500	100	50	8048	2.8	1.4745						30min FTS
115	0.85	0	200(8)	400	500	100	50	10620	8.6	1.4549						30min FTS, RI Wafer
116	0.85	0	200(8)	400	500	100	50	9073	3.5	1.4524						30min FTS
117	0.85	0	200(8)	900	500	100	50	14852	2.3	1.4384						30min FTS
118	0.85	0	200(8)	900	500	100	50				2.55	0.0343	0.0096	0.0096	0.0096	30min FTS, Cap
119	0.85	0	200(8)	900	500	100	50				2.76					30min FTS, Cap
120	0.85	0	200(8)	900	250	100	50	11633		1.4334						30min FTS, Cap
121	0.85	0	200(8)	900	250	100	50	9812		1.3954						30min FTS, Cap
122	0.85	25	175(8)	900	250	100	50	10515	1.381	1.3807		0.0363	0.0094	0.0751	0.0751	30min FTS, Stress=9.78E8T
123	0.85	15	150(8)	900	250	100	50	10515	1.381	1.3807		0.0363	0.0094	0.0751	0.0751	30min FTS, Stress=7.31E8T
124	0.85	15	150(8)	900	250	100	50	10515	1.381	1.3807		0.0363	0.0094	0.0751	0.0751	30min FTS, Stress=5.32E8T
125	0.85	75	125(8)	900	250	100	50	10640	1.387	1.3807		0.034	0.0051	0.0556	0.0556	30min FTS, Stress=5.041E8T
126	0.85	100	100(8)	900	250	100	50	11727	1.3587	1.3587		0.0285	0.0042	0.0344	0.0344	30min FTS, Stress=5.74E8T
127	0.85	25	175(8)	900	250	100	50	12588	1.3481	1.3481		0.0293	0.0056	0.0336	0.0336	30min FTS, Stress=8.77E8T
128	0.85	25	175(8)	900	250	100	50	9206		1.3718		0.0331	0.0051	0.0466	0.0466	30min FTS, Stress=8.02E8T
129	0.85	75	125(8)	900	250	100	50				2.414					30min FTS
130	0.85	100	100(8)	900	250	100	50				2.49					30min FTS
131	0.85	25	175(8)	900	250	100	50				2.41					30min FTS
132	0.85	25	175(8)	900	250	100	50				2.48					30min FTS
133	0.85	15	150(8)	900	250	100	50				2.43					30min FTS
134	0.85	30	170(8)	900	250	100	50				2.45					30min FTS

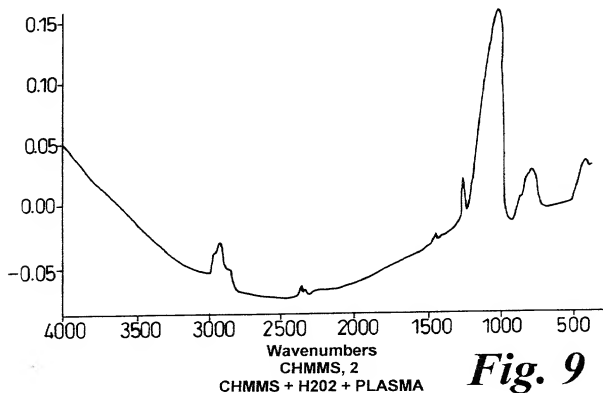
Fig. 7 (Part 3 of 3)

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1.) 800CHMMS, 0.4g/min H2O2, 900mT, 250W as deposited

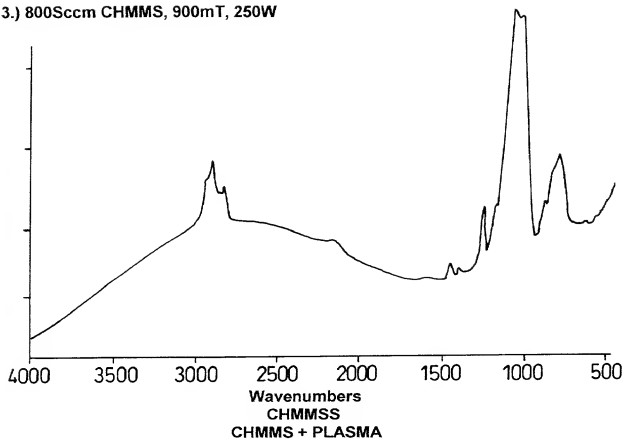
**Fig. 8**

2.) 800Sccm CHMMS, 0.4g/min H2O2, 900mT, 500W

**Fig. 9**

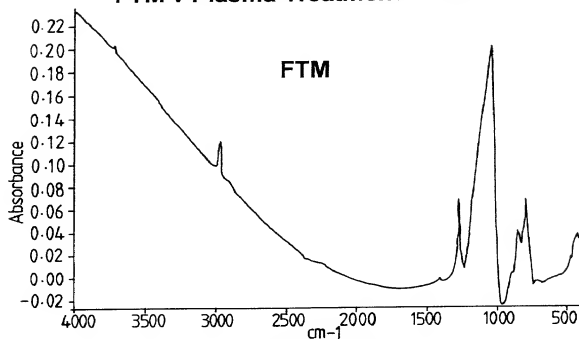
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3.) 800Sccm CHMMS, 900mT, 250W

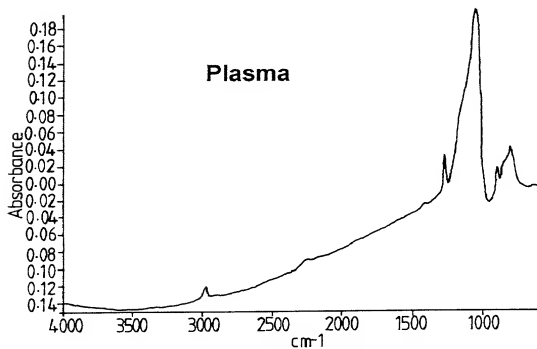
***Fig. 10***

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TMS / O₂ Process
FTM v Plasma Treatment – FTIR



SiC/SiO :	0.0504
SiH/SiO :	0.0279
CH/SiO :	0.0279



SiC/SiO :	0.026
SiH/SiO :	0.019
CH/SiO :	0.0220

Fig. 11

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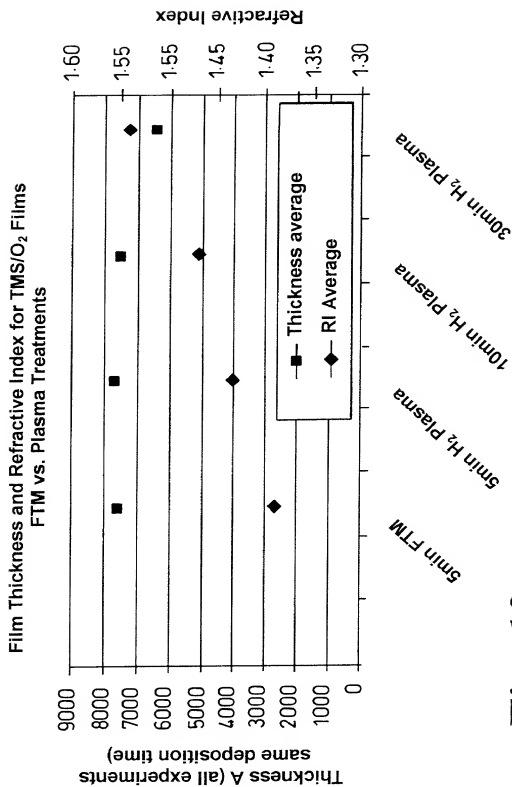
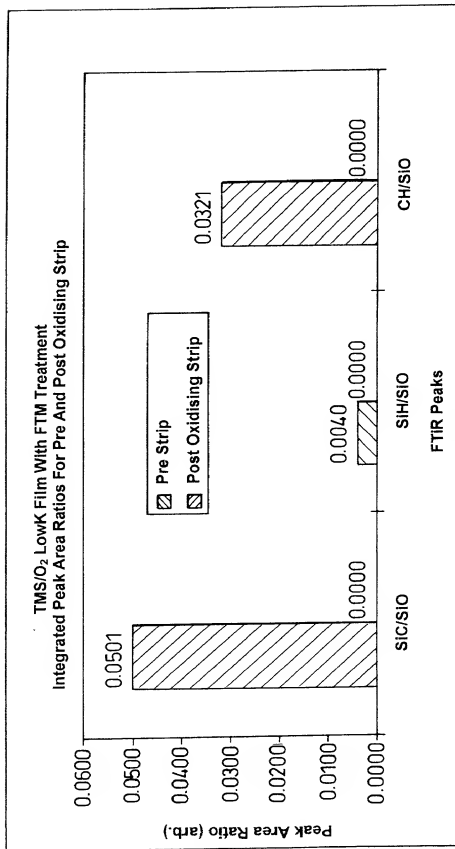


Fig. 12

TMS / O₂ Process FTM Treatment – FTIR – oxidising strip resistance



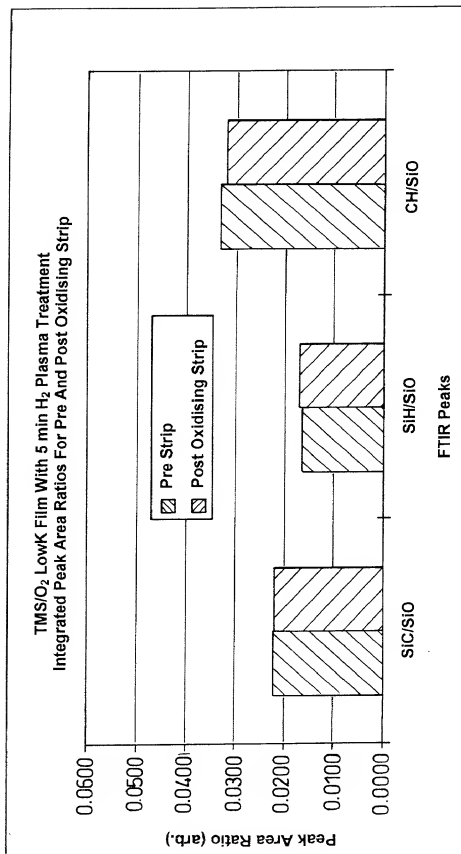
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Fig. 13

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TMS / O₂ Process
FTM Treatment – FTIR – oxidising strip resistance

**Fig. 14**

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TMS / O₂ Process
FTM Treatment – FTIR – oxidising strip resistance

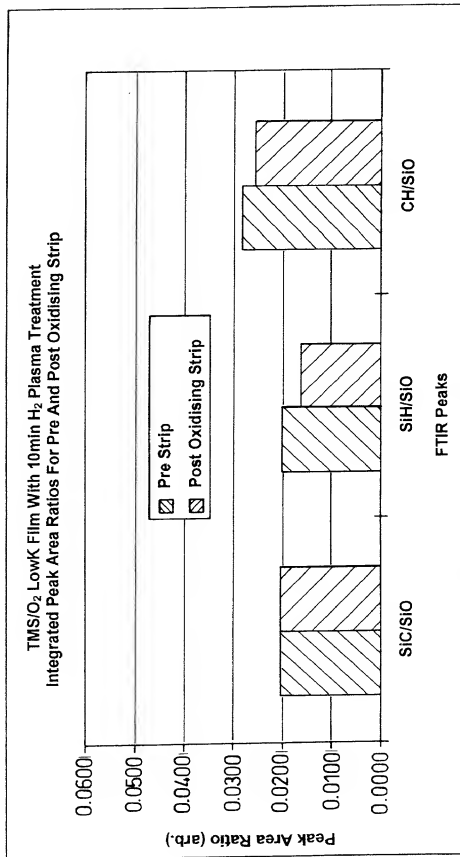


Fig. 15

TMS / O₂ Process FTM v Treatment stress – oxidising strip resistance

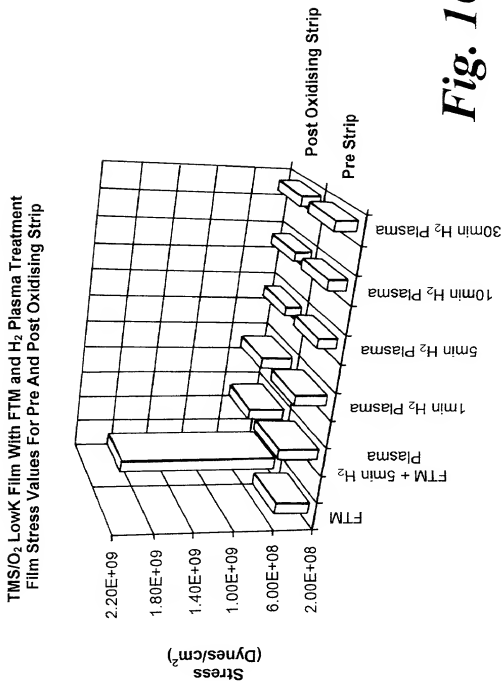


Fig. 16

TMS / O₂ Process Plasma Treatment – Dielectric constant

Dielectric Constant Values For TMS/O₂ Films
FTM and H₂ Plasma Treatments

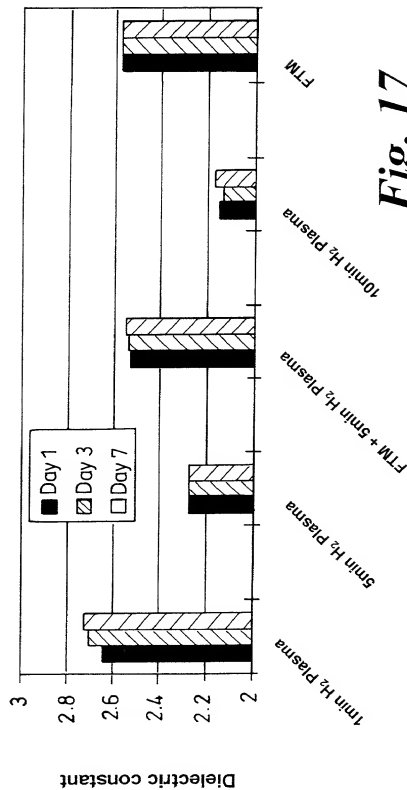


Fig. 17

Dielectric Constant For TMS/O₂ Films
FTM and H₂ Plasma Treatments

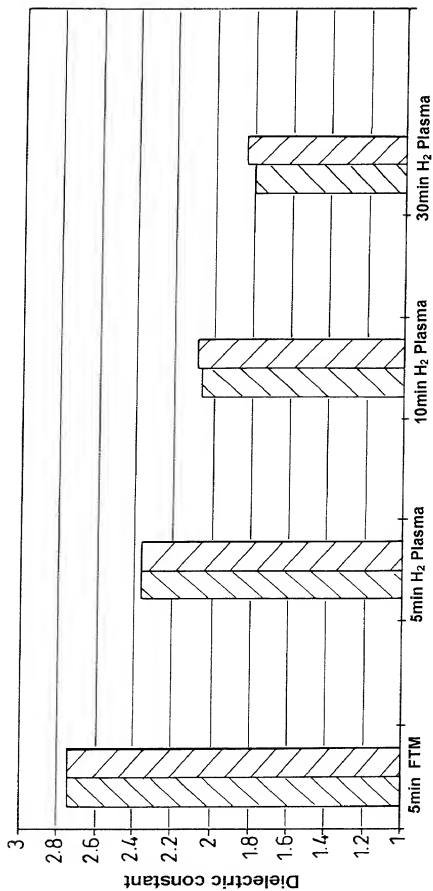
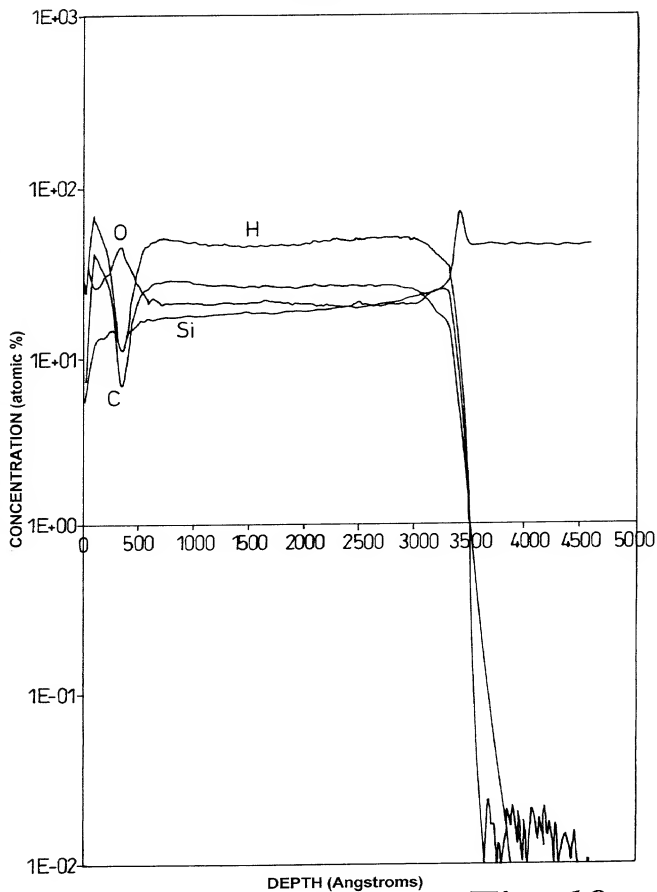


Fig. 18

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**Fig. 19**

DECLARATION AND POWER OF ATTORNEY FOR U.S. PATENT APPLICATION

(X) Original () Supplemental () Substitute () PCT () Design

As a below named inventor, I hereby declare that: my residence, post office address and citizenship are as stated below next to my name; that I verily believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

TITLE: METHOD AND APPARATUS FOR FORMING A FILM ON A SUBSTRATE

of which is described and claimed in:

() the attached specification, or

() the specification in the application Serial No. _____ filed _____

and with amendments through _____ (if applicable), or

(X) the specification in International Application No. PCT/GB00/02301, filed 26 JUNE 2000

and as amended on _____ (if applicable).

I hereby state that I have reviewed and understand the content of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge my duty to disclose information of which I am aware which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (and §172 if this application is for a Design) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

COUNTRY	APPLICATION NO.	DATE OF FILING	PRIORITY CLAIMED
GREAT BRITAIN	9914879.3	26 JUNE 1999	YES
GREAT BRITAIN	9922693.8	25 SEPTEMBER 1999	YES
GREAT BRITAIN	9922691.2	25 SEPTEMBER 1999	YES
GREAT BRITAIN	9922801.7	28 SEPTEMBER 1999	YES
GREAT BRITAIN	0000780.7	14 JANUARY 2000	YES

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION SERIAL NO.	U.S. FILING DATE	STATUS: PATENTED, PENDING, ABANDONED

And I hereby appoint Adam C. Volentine, Reg. No. 33,289, and the firm of JONES VOLENTINE, L.L.C., jointly and severally, attorneys to prosecute this application and to transact all business in the U.S. Patent and Trademark Office connected therewith.

I hereby authorize the U.S. attorneys named herein to accept and follow instructions from WYNNE-JONES, LAINE & JAMES, as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. attorneys and myself. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys named herein will be so notified by me.

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400

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500

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I further declare that all statements made herein of my own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

1st Inventor K. S. GILES Date 27/2/01
Katherine GILES

2nd Inventor Knut BEEKMANN Date 22/2/01
Knut BEEKMANN

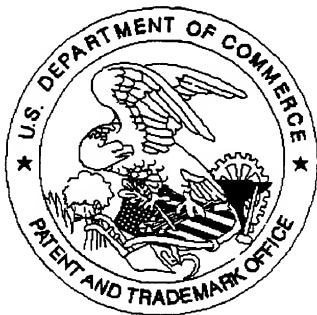
3rd Inventor Christopher David DOBSON Date 21/2/01
Christopher David DOBSON

4th Inventor John MACNEIL Date 22/2/01
John MACNEIL

5th Inventor Antony Paul WILBY Date 28/2/01
Antony Paul WILBY

Applicant Reference No.: DBN.104 Atty Docket No.: WLJ.072

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